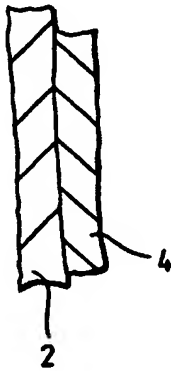


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(54) Title: COMPOSITE FABRIC			
(57) Abstract <p>A composite water-vapour-permeable fabric used in garments, footwear, hats, gloves, etc., comprises a laminate of a sheet of expanded polytetrafluoroethylene (PTFE) membrane (2) and a layer of non-expanded porous PTFE (4) formed thereon. The non-expanded PTFE is preferably a sintered network of granular-type PTFE particles fused together and formed in situ on the expanded PTFE membrane.</p>			
			

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COMPOSITE FABRICTECHNICAL FIELD

The present invention relates to a composite fabric formed from polytetrafluoroethylene (PTFE), and to garments, shoes etc made therefrom.

The term "fabric" normally includes woven or non-woven fibre-containing materials. However, the composite fabric of the present invention whilst being employable in applications in which fabrics are normally employed (e.g. clothing, footwear, hats, gloves, coverings, covers hangings etc.), does not necessarily possess a fibrous nature.

BACKGROUND

It is known that garments may be produced which are waterproof and breathable by including in the garment a membrane formed of expanded polytetrafluoroethylene (ePTFE) as disclosed for example in patent specification US 3,953,566. The ePTFE membrane is formed by expanding a film formed from "fine powder" polytetrafluoroethylene so as to form a porous structure. The ePTFE membrane is resistant to ingress of liquid water under moderate water entry pressures. On the other hand, the membrane is breathable to allow water vapour from the wearer to pass through the membrane, which prevents

the inside of the garment from becoming damp and uncomfortable. A waterproof breathable material is available from W.L. Gore & Associates under the trademark GORE-TEX and comprises an expanded PTFE membrane coated with a thin layer of a hydrophilic polyurethane material, such as is disclosed in patent specification US 4,194,041. Such coated membrane materials have been widely used for the production of waterproof breathable garments, and are particularly beneficial for high exertion activities where a high moisture vapour transmission rate is desirable.

It is an object of the present invention to provide such a waterproof breathable material for use in garments, shoes etc., having improved properties.

British published patent application 2242431 discloses a sintered porous polytetrafluoroethylene structure used as a filter in industrial filtration. The porous polytetrafluoroethylene material is produced by fusing particles of polytetrafluoroethylene such as to form a sintered porous integral network of interconnected particles.

Patent publication W096/40510 discloses a porous composite which comprises a layer of expanded polytetrafluoroethylene (PTFE) membrane, and a layer of non-expanded porous PTFE attached thereto. The non-expanded porous PTFE layer may be composed of sintered porous PTFE. This patent specification

discloses that the laminate may be used for oiling and cleaning high temperature fuser rolls in a photocopying machine, or as a filter. There is no disclosure that the laminate may have useful properties when employed as a fabric for the creation of garments etc.

SUMMARY OF THE INVENTION

It has now been surprisingly found that such a composite fabric comprising an ePTFE membrane and a layer of non-expanded PTFE attached thereto has particularly advantageous properties, including improved abrasion resistance and resistance to fracture whilst at the same time exhibiting good moisture vapour transmission rates.

Thus, one aspect of the present invention provides a composite fabric which comprises a polytetrafluoroethylene laminate comprising:

- a sheet of expanded polytetrafluoroethylene (PTFE) membrane; and
- a layer of non-expanded porous polytetrafluoroethylene (PTFE) attached to the expanded membrane sheet.

The layer of non-expanded porous PTFE may be a sintered material which is generally made by a sintering process wherein PTFE solids are heated to high temperature to form a porous matrix. One such

material is available under the Zitex trademark (Norton Chemplast, New Jersey, USA) and comprises fibrous PTFE wherein PTFE fibres are bonded into a porous matrix. Such materials may be formed by mixing cellulosic or proteinaceous materials with PTFE and heating in oxygen to high temperatures to burn out or carbonise cellulosic or proteinaceous material and to sinter the PTFE (see US patent 3,775,170).

However, in a particularly preferred embodiment the layer of non-expanded porous PTFE is a sintered porous PTFE formed from PTFE particles, comprising granular-type PTFE particles, fused together such as to form a porous integral network of interconnected particles. The PTFE particles used to form the porous network are generally wholly or partially made-up of granular-type PTFE particles, though other types of PTFE particles may also be included. The nature of "granular-type" PTFE is discussed later.

By the term "sintered" (and "presintered") is meant that the PTFE under consideration has been heated to above its melting point, which is about 343°C for pure unmodified PTFE. By the term "unsintered" is meant that the PTFE has not been heated to above its melting point.

The composite fabric of the present invention has been found to possess properties which particularly suit it for use as a fabric. For example, the

thickness of the composite fabric may be adjusted to provide the feel and handle normally associated with a woven or non-woven fabric material, whilst at the same time maintaining other desirable properties such as high water vapour transmission rates. The presence of the non-expanded PTFE layer also appears to impart enhanced abrasion resistance over the ePTFE membrane alone, and the abrasion resistance is usually found to be improved on both sides of the composite fabric. Generally speaking, the composite fabric of the present invention exhibits improved desirable fabric properties without sacrificing waterproofness and breathability. It is particularly useful in areas of high abrasion, and also exhibits good crush resistance.

Water-resistant materials which resist liquid water penetration are well known to persons skilled in the art and the term is to be construed accordingly. Clearly, the degree of water-resistance required in a so-called waterproof garment depends upon the severity of the climatic conditions to which it is subjected. A suitable test of water-resistance (Suter Test) is described herein. A practical indication of water-resistance is that liquid water is not forced through the sample by a pressure of 1.4lbs per square inch (0.1kg per cm²), or more typically 2.0lbs per square inch (0.14 kg/cm²).

The benefit of a water-vapour-permeable material is that perspiration from the wearer's body is allowed to escape from within the garment by passage through the material, thus preventing build up of liquid water within the garment and consequent damp and uncomfortable feeling. In order to be considered as water-vapour-permeable, the composite fabric should generally have a water-vapour-permeability of at least 1,000, for example 1500 to 50,000 g/m²/day, particularly 3000 to 35,000 g/m²/day and especially 3000 to 15,000 g/m²/day.

The composite fabric as described above will generally be a porous material allowing the passage of air or other gas therethrough. In practice, it is found that the layer of non-expanded PTFE does not hinder to any great degree the air permeability of the composite fabric as compared to the permeability of the ePTFE membrane itself. In fact, the permeability is largely dependent upon the permeability of the ePTFE membrane itself. Typically, the composite fabrics have Gurley numbers in the range 10-40 s/100cm³, preferably 20-30 s/100cm³.

It is found that the abrasion resistance (e.g. using a Martindale abrasion tester) of the composite fabric of the invention is much enhanced over the abrasion resistance of the ePTFE membrane itself. Similarly, there was an improvement in impact

resistance of the composite fabric (for example, measured as fracture resistance herein) in comparison to the ePTFE membrane alone. Thus, the mechanical properties of the composite fabric are enhanced in comparison to the properties of the ePTFE membrane alone.

The composite fabric has excellent mechanical properties, particularly at elevated temperatures such as 200°C where other known materials may be subject to heat degradation. The composite fabric being formed substantially from polytetrafluoroethylene also exhibits excellent chemical resistance. The composite fabric can thus be sterilised by chemical treatment.

The composite fabric also exhibits excellent dimensional stability and has much reduced tendency to shrink at high temperatures (e.g. 250°C). The composite fabric does not tear easily.

The thickness of the porous composite material is generally in the range 50 to 2000 microns, particularly 150 to 1000 microns. The expanded PTFE membrane may have a thickness of less than 30 microns (for example, down to 5 microns), but is typically 30 to 500 microns, particularly 50-150 microns. The layer of non-expanded porous PTFE usually has a thickness up to and above 2000 microns, especially in the range 10-1000 microns, particularly 25-500 microns, especially 50-250 microns.

Thus, it is surprisingly found that the composite fabrics of the present invention can be formed in thicknesses which give good mechanical properties yet at the same time provide the feel and handle of a fabric, for example without being too stiff. The layer of non-expanded porous PTFE tends to give the composite fabric a soft feel. When preparing composite fabrics having a relatively thin layer of non-expanded porous PTFE, it is advantageous to employ small particle size PTFE in the production process, so as to provide a fine surface finish.

One face of the composite fabric may be textured. Such texturing may be effected by the use of a spray application technique to form the non-expanded layer as described hereafter.

Although the invention is primarily concerned with a composite fabric which comprises two layers, viz; an expanded PTFE membrane and a layer of non-expanded (e.g. sintered) porous PTFE, it is also possible to form the material as a multiplicity of layers, which are formed of alternating layers of expanded PTFE membrane and non-expanded porous PTFE. A particularly useful composite fabric comprises layers of non-expanded PTFE on both sides of the ePTFE membrane.

Generally speaking, the layers may be bonded together in any suitable manner known in the art, such

as by the use of adhesives, by stitching etc. Where adhesives are used, the pattern of adhesive should preferably be a discontinuous pattern, such as a pattern of dots or lines so as to avoid the composite fabric from becoming too stiff. However, certain techniques of bonding the layers together, such as pressure bonding, are unsuitable, since the application of a pressure which is sufficient to lead to bonding may lead to crushing and distortion of the expanded PTFE membrane. Moreover, the use of an intervening adhesive or heat-bonding interlayer, constitutes a limitation on the properties of the overall porous composite material. Thus, parameters such as heat stability and chemical resistance may be limited by the properties of the adhesive or other material used to bond the two layers.

However, in a particularly preferred embodiment the two layers may be integrally formed without the use of any intervening adhesive or other bonding material. In this way, a composite fabric is achieved which is formed entirely of polytetrafluoroethylene and which therefore has the overall properties of polytetrafluoroethylene without limitation by other components present. In particular, a layer of sintered non-expanded porous PTFE may be formed in situ on the expanded PTFE membrane. It has been found possible to form the sintered porous PTFE layer

directly on the expanded PTFE membrane by the application of a liquid suspension comprising granular-type PTFE particles, followed by baking at elevated temperatures so as to fuse together the granular-type PTFE particles and to form a porous integral network of interconnected particles. It has been found that the liquid dispersion can be arranged such as to wet the surface of the expanded PTFE membrane and to form a continuous liquid layer thereon without any discontinuities. When the granular-type PTFE layer is sintered at elevated temperatures, the layer of sintered porous PTFE becomes securely attached to the expanded PTFE membrane. It is normally difficult to heat-weld PTFE to PTFE by the simple application of high temperature. Bonding occurs at atmospheric pressure without the application of any elevated pressures which might otherwise lead to crushing of the expanded PTFE membrane. Also the application of the layer of sintered porous PTFE by a liquid application technique does not appear to substantially effect the porosity of the expanded PTFE membrane. It must therefore be assumed that no interfacial barrier is created between the sintered porous PTFE layer and the expanded PTFE membrane, nor are the pores of the expanded PTFE membrane blocked by the application of the sintered porous PTFE layer.

Thus, the present invention advantageously allows

the production of a composite fabric which is composed substantially entirely of polytetrafluoroethylene, whereby the maximal properties of polytetrafluoroethylene may be enjoyed. However, this does not preclude the inclusion of small amounts of modifiers as described herein.

If required, a layer of sintered porous PTFE formed from a liquid dispersion may be formed in situ between two expanded PTFE membranes, followed by baking at elevated temperature, so as to form a unitary multiple layer all-PTFE composite structure. Conversely, layers of sintered porous PTFE may be formed on either side of an expanded PTFE membrane (for example, by spraying and baking).

This fabrication technique is essentially brought about by the different methods of preparation of the expanded PTFE membrane and the preparation of the sintered porous PTFE layer. The former is generally produced by extrusion and stretching of a film; whereas the latter is produced from a coating of a liquid dispersion.

The expanded PTFE membrane can be made using a number of processes, including the formation of an expanded network of polymeric nodes and fibrils in accordance with the teachings of US patents 3,953,566, 3,962,153, 4,096,227 and 4,187,390. Generally, expanded PTFE membrane is made by blending a

dispersion of so-called fine powder PTFE with hydrocarbon mineral spirits. The lubricated PTFE is compacted and ram extruded to form a tape. The tape can then be rolled down to a desired thickness and subsequently dried by passing the tape over heated drying drums. The dried tape can then be expanded both longitudinally and transversely at elevated temperatures. The expanded porous PTFE membrane generally has a pore size in the range 0.02 to 15 microns as measured by the bubble point method described herein. The choice of pore size may have an effect on the moisture vapour transmission rate of the composite fabric.

In one embodiment, the expanded PTFE membrane is formed into a fabric by twisting tapes of the membrane and weaving these into a fabric (such a material is available from W.L. Gore & Associates, Inc. under the RASTEX trademark). This fabric may be laminated (e.g. by heat bonding) to an expanded PTFE membrane to give improved mechanical properties. Alternatively, the layer of non-expanded porous PTFE may be applied onto the fabric alone.

The non-expanded porous PTFE layer may be a sintered material produced as described in patent specification GB2242431. The material is formed from one or more grades of granular-type polytetrafluoroethylene. As is well known, PTFE is

produced in two distinct types which are so called "granular" PTFE and so called "fine powder" PTFE. Fine powder PTFE is employed to produce the expanded PTFE membrane discussed above. On the other hand, the sintered non-expanded porous PTFE layer is produced from granular-type PTFE. These materials have quite different properties.

By the term "fine powder type PTFE" is meant that type of PTFE produced by the emulsion polymerisation technique. This technique produces a resin that cannot be ram extruded but which must be extruded by the paste extrusion method where the resin must first be mixed with a lubricant. The term "fine powder" is a term of art in the PTFE field and refers to the type of PTFE. It has no relationship to particle size.

Both the term "granular type" and "fine powder type" PTFE include herein homopolymer tetrafluoroethylene and modified PTFE, so-called because the homopolymer is modified by copolymerisation with a copolymerisable ethylenically unsaturated comonomer in a small amount of less than 2% by weight of copolymer. These copolymers are called "modified" because they do not change the basic character of homopolymer PTFE, and the copolymer remains non-melt processable just as the homopolymer. Examples of comonomers include olefins such as ethylene and propylene; halogenated olefins such as

hexafluoropropylene (HFP), vinylidene fluoride and chlorofluoroethylene; or perfluoroalkyl vinyl ethers such as perfluoropropyl vinyl ether (PPVE).

The sintered non-expanded porous PTFE may be produced from a dispersion of granular-type PTFE particles in a liquid. The granular-type PTFE used in this preparation may be unsintered or may have been pre-sintered. The sintering process modifies the characteristics of the granular-type PTFE material. One particular embodiment of the present invention employs unsintered PTFE material; however mixtures of sintered and unsintered material may also be used in other embodiments. Teflon granular-type resin grades 7A (unsintered) and 9B (sintered) are available from DuPont Speciality Polymers Division, Wilmington, USA. Generally speaking, the sintered non-expanded porous PTFE may be produced from 0-100% unsintered PTFE (e.g. grade 7A) and conversely 100-0% sintered PTFE (e.g. grade 9B). Where the sintered porous PTFE is formed from a mixture of sintered and unsintered granular-type PTFE particles, it is preferred that the unsintered PTFE predominate since this leads to a material having good strength. The inclusion of sintered PTFE particles tends to increase the porosity of the sintered porous PTFE layer produced.

The granular-type PTFE particles may have a particle size in the range 1 to 600 microns,

especially 5 to 500 microns, particularly 10 to 300 microns.

The unsintered granular-type PTFE will ordinarily have a particle size of between 1 and 300 microns, particularly 10 and 150 micron (mean size of about 10 to 35 microns). One commercial grade of unsintered granular-type resin is available from the DuPont company as Teflon 7A as mentioned above; and is preferably milled to reduce its particle size for example to a mean size of 10 to 20 microns. Another grade, having elongated fibrous particles, is available from DuPont with the trade name Teflon 7C. The granular-type resin or resins (whether unsintered or sintered) may also be modified by the inclusion of a small amount of a comonomer (such as hexafluoropropylene or perfluoropropyl vinyl ether) typically in an amount up to 1% or up to 2% by weight. An unsintered modified PTFE is Teflon 70J available from Mitsui Fluorochemical. It is modified PTFE in which the comonomer is perfluoropropyl vinyl ether (PPVE). It can be presintered before use.

Unsintered granular PTFE tends to be made of soft particles which can "pack" together to form a fairly strong web when sintered having small pore sizes. For example, Teflon 7A has a tensile strength of 471.4 N/CM² and a mean pore size of 2.01 micron, when a mean particle size of approximately 35 microns is fused

into a network.

On the other hand, sintered granular PTFE is composed of hard, substantially noncompactable particles. When baked above the melt temperature, only weak inter-particle connection is obtained and leads to large pore sizes. For example, sintered granular-type PTFE is available from the DuPont company under the tradename Teflon 9B. It has a specific strength of 79N/cm^2 and a mean pore size of 6.04 micron when milled particles of 40 micron size are fused into a network.

The granular-type PTFE particles (whether sintered or unsintered particles, or a mixture of both) used to produce the sintered non-expanded porous PTFE may have admixed therewith materials selected from the class consisting of

- (i) unsintered fine powder PTFE (which may itself be modified or unmodified),
- (ii) particles of a thermoplastic fluorinated organic polymer,
- (iii) particles of a low molecular weight PTFE micropowder produced by irradiation, and
- (iv) mixtures thereof;

present in an amount of between 1 and 20% by weight of solids.

Unsintered fine powder PTFE is available from a number of sources, eg The DuPont Company, ICI or

Daikin, and may be used either in particle form or in the form of a liquid dispersion thereof. A modified fine powder PTFE containing hexafluoropropylene comonomer is available from ICI (primary particle size 0.2 to 0.4 microns) as CD509 and modified PTFE containing perfluoropropyl vinyl ether is also available. Such modified resins generally contain upto 1% or upto 2% by weight of the modifier.

Examples of the thermoplastic fluorinated organic polymers include copolymers of tetrafluoroethylene and hexafluoropropylene (commonly called fluorinated ethylene-propylene copolymer or FEP), and of tetrafluoroethylene and perfluoroalkyl vinyl ether (when the ether is perfluoropropyl vinyl ether the copolymer is commonly called PFA).

Micropowders produced by irradiation are available from DuPont.

Particles of an organic or inorganic filler material may also be included. Examples of fillers include carbon, activated carbon, glass, chromium oxide, titanium oxide, chopped expanded PTFE, silica dioxide, and the like. In other words, virtually any filler can be employed to add specific properties to the composition. The amount of filler can be as high as 60% or more based on weight of composition.

Where the sintered non-expanded porous PTFE is formed of a mixture of sintered granular-type

particles, together with a "softer" material such as unsintered granular-type PTFE or any of the materials (i) to (iv) above, it is believed that the softer materials form moieties which link the harder sintered particles to provide increased inter-particle connection strengths. Non-expanded PTFE formed solely of hard sintered granular-type PTFE particles tends to have relatively poor strength, and poor adhesion to the expanded PTFE membrane. Adhesion to the expanded PTFE membrane is increased by increasing the proportion of unsintered granular resin, by including a modifier in the granular resin, or by including any of the softer materials.

The overall density of the composite fabric is generally in the range 0.5 to 1.2, typically 0.7 to 1.0 g/cm³ measured as described herein. In comparison, pure non-porous solid PTFE typically has a density of 2.16 g/cm³. Generally, the expanded PTFE membrane will have a porosity in the region 50-98%, generally 70-95%. The density of the sintered porous PTFE layer measured as described herein is usually in the range 0.5 to 1.8, for example 0.6 to 1.5, typically 0.7 to 1.2 g/cm³ (corresponding to porosities of 77 to 16%, 72 to 30% and 68 to 44% respectively).

In fact, the properties of the expanded PTFE membrane and the sintered porous PTFE layer differ markedly as regards porosity and pore size. Generally

speaking, the expanded PTFE has a relatively high porosity and smaller pore size; whereas the sintered porous PTFE has a relatively low porosity and a larger pore size. Typical values of materials for use in the present invention are as follows.

	<u>Porosity</u>	<u>pore size</u> <u>(microns)</u>	<u>Bubble point</u> <u>(pounds/in²)</u>
expanded PTFE	50-98%	0.02-10*	40-0.4
sintered porous PTFE	30-80% (eg.30-70%)	0.5-20** (eg.2-6)	5-0.1 (eg.1-0.6)

* maximum pore size as determined by Bubble Point method D1.

** mean pore size as determined by Coulter Porometer method D2.

A further aspect of the present invention provides a method of forming the composite fabric which comprises providing an expanded PTFE membrane; and forming thereon a layer of sintered non-expanded porous PTFE attached to the expanded PTFE membrane, the sintered porous PTFE being formed from particles of granular-type PTFE fused together such as to form a porous integral network of interconnected particles.

As mentioned above, the layer of sintered porous PTFE is generally formed by coating the expanded PTFE membrane with a liquid dispersion comprising particles of granular-type PTFE and baking at an elevated temperature such as to form a porous integral network.

The liquid dispersion can be applied by any suitable liquid coating technique, such as roller coating or by using a doctor blade, so as to apply a continuous coating of uniform depth over the expanded PTFE membrane. However, in a preferred embodiment, the liquid PTFE dispersion is applied onto the expanded PTFE membrane by spraying.

The dispersion will contain suitable surfactants and thickening agents to enable it to wet and continuously coat the expanded PTFE membrane.

If desired, a stabilised aqueous dispersion of the (i) fine powder or the (ii) thermoplastic fluorinated organic polymer can be mixed with the granular-type PTFE mixture in an aqueous liquid (eg. of water and alcohol, for example isopropanol) and the ingredients can be co-coagulated. This results in the much smaller sized fine powder resin polymer or the thermoplastic polymer particles congregating about the surface of the much larger size granular-type particles. This coagulated product can then be dispersed in water for spray coating or dip coating.

The liquid coating is then dried and baked at elevated temperature. Usually, a preliminary step involves heating slowly to 100°C in order to dry off water and any other volatiles, and holding at that temperature for a short period of time. Thereafter, the temperature is raised progressively up to 330 to

385°C (e.g. 340 to 370°C) in order to allow sintering and fusion of the PTFE particles to occur.

At these high temperatures, the expanded PTFE membrane is not dimensionally stable and tends to stretch if held under an applied load, or to shrink if there is no load. Therefore, the expanded PTFE membrane is generally held in a frame, or stenter (for a continuous process) so as to prevent shrinkage or elongation during the production of the sintered porous PTFE layer.

The composite fabric as discussed above may be subject to further treatments. Other layers may also be laminated thereto in an essentially conventional manner.

For example, the expanded PTFE membrane, and optionally the non-expanded porous PTFE layer may be impregnated with a hydrophobic impregnant, such as a low molecular weight perfluoro compound, for example a perfluoroalkyl acrylate or methacrylate. Such impregnation enhances the water-resistance of the composite fabric.

As discussed above, it is known to apply a layer of hydrophilic material, such as a polyurethane, onto expanded PTFE membranes in conventional manner as described in patent specification US 4,194,041. Such layers or coatings protect the expanded PTFE membrane from fats and oils from the body of the wearer, yet

are at the same time moisture vapour permeable so as to allow the transmission of water vapour therethrough. Such hydrophilic layers may be applied to the composite fabric of the present invention and generally result in a material which is no longer gas or air permeable. The hydrophilic layer or coating may be applied either to the expanded PTFE membrane (e.g. for booties) or to the layer of non-expanded porous PTFE (e.g. for garments) or to both.

The composite fabric of the invention may have laminated thereto other fabric layers, such as face fabrics or liners in essentially conventional manner. Face fabrics are typically woven nylon or polyester fabrics. Liners are typically lightweight open weave fabric materials whose function is to protect the composite fabric of the present invention.

The material of the present invention may be used to produce garments, hats, gloves, shoes etc.

An important feature of the composite fabrics of the present invention is their ability to be seam sealed. This is carried out in order to seal the stitched seams of a water-resistant garment to prevent liquid water entering through the stitching holes. It is accomplished by applying a tape coated with a heated hot melt adhesive under pressure over the inside of the seam and bonding thereto. The materials of the present invention can be seam-sealed by

applying the hot melt adhesive either to the expanded PTFE membrane or to the non-expanded porous PTFE layer. The composite fabric of the present invention has good seam sealing properties and good adhesion of the seam sealing tape.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings wherein;

Figure 1 is a cross-section to an enlarged scale of a composite fabric according to the present invention;

Figure 2 is a cross-section of a composite fabric according to the invention having two layers of sintered porous PTFE on either side of the expanded PTFE membrane;

Figure 3 is a cross-section of a composite fabric laminated to a face fabric; and

Figure 4 is a cross-section of a composite fabric carrying a hydrophilic coating.

Figure 1 shows a porous composite fabric 1 of the present invention to an enlarged scale. The composite fabric comprises at least two layers 2 and 4. Layer 2 is composed of an expanded polytetrafluoroethylene (PTFE) membrane, a material which is available in a variety of forms from W.L.

Gore & Associates Inc. of Elkton, MD, USA, under the trademark Gore-Tex. The expanded PTFE membrane is typically produced by blending a PTFE fine particle dispersion with hydrocarbon mineral spirits, followed by compaction and ram extrusion through a die to form a tape. The tape may then be rolled down to a desired thickness and dried by passing over heated drying drums. The dried tape can then be expanded both longitudinally and transversely at elevated temperatures at a high rate of expansion, so as to form a porous expanded PTFE membrane.

In an alternative embodiment, the layer 2 is composed of expanded PTFE membrane in the form of twisted tape, which has been woven into a fabric. One such fabric is available under the Rastex trademark from W.L. Gore & Associates Inc.

The second layer 4 of PTFE material is formed of a sintered PTFE material made in a different way. The sintered material is produced by forming a liquid suspension comprising granular-type PTFE particles. The granular-type PTFE particles may be pre-sintered, unsintered or partially sintered, or may be a mixture of these various forms of granular-type PTFE (including other forms mentioned herein). The suspension is then sprayed in one or more layers onto a substrate until the desired thickness is achieved. The sprayed material is dried in an oven by taking the

material through a predetermined drying and baking regime up to elevated temperatures (e.g. 350-385°C), as described in more detail later. This leads to the production of a porous sintered structure wherein the particles of granular-type PTFE become fused together to form a porous integral network of interconnected particles. This material is characterised by a particularly large pore size in relation to the expanded PTFE membrane (for a given porosity). Generally, the sintered porous PTFE material is produced in the same or greater thicknesses than the expanded PTFE. The sintered porous PTFE has excellent dimensional stability.

The porous composite material is advantageously formed by spraying (or otherwise applying, such as by means of a doctor blade) the liquid PTFE particle suspension directly onto the expanded PTFE membrane which thereby acts as the substrate. Generally the bond strength between surfaces of PTFE materials is poor without the use of surface treatments and/or adhesives, but it has been found that not only is it possible to apply the aqueous liquid suspension directly onto the expanded PTFE membrane, but that after baking, a good bond is formed between the two layers. This not only provides a convenient fabrication technique, but also produces a porous composite material which is composed entirely of PTFE

and therefore is a material whose overall properties are not limited by the presence of any other agent of inferior properties.

However, expanded PTFE membrane tends to shrink (or to stretch if under tensile load) at the elevated temperatures required for baking the sintered porous PTFE material. For this reason, it is necessary to hold the expanded PTFE membrane in such a way as to maintain its original dimensions during the baking process. One way of approaching this is to hold the expanded PTFE membrane in a frame (where single pieces of material are to be produced) or by means of a stenter in the case of a continuous production facility.

Another benefit of forming the sintered porous PTFE layer directly on the expanded PTFE membrane, is that restrictions on the properties of the sintered porous PTFE material which may arise from skinning of the outer surface thereof are mitigated, since there is effectively no free surface at the interface between the membrane and the sintered porous PTFE layer. The ability of air and moisture vapour to flow across the interface between the porous expanded PTFE membrane and the sintered porous PTFE layer is good.

In an alternative less preferred fabrication method, it is possible to preform the expanded PTFE membrane and the layer of sintered porous PTFE in

separate fabrication steps, and thereafter to laminate the one to the other by conventional lamination technology. Such lamination technology includes the use of continuous or discontinuous intermediate adhesive layers using a variety of adhesives known for the purpose. In the case of an adhesive which is impermeable to liquid, the adhesive layer would normally be in the form of a discontinuous pattern, such as a pattern of dots or lines. A disadvantage of the use of adhesives is that generally speaking their properties, such as high temperature resistance and chemical resistance are generally inferior to those of either the expanded PTFE membrane or the sintered PTFE layer, so that the overall properties of the porous composite material are correspondingly degraded.

Figure 2 shows a composite fabric forming a further embodiment of the present invention wherein two layers 4, 5 of sintered porous PTFE are applied, one on either side of the expanded PTFE membrane 2. This may be achieved by applying the liquid PTFE suspension onto both sides of the expanded PTFE membrane prior to baking, generally by a spray application technique. Alternatively, one of the layers 4, 5 may be applied to one side of the PTFE membrane and then baked, before applying a further layer of liquid suspension on the other side of the expanded PTFE membrane followed by a second baking

cycle. The composite fabric according to this embodiment has a layer of sintered porous PTFE on either face and therefore provides a composite fabric having particular handle properties. Moreover, the expanded PTFE membrane is well protected from damage by external mechanical forces, such as abrasion, creasing etc.

Figure 3 shows a composite fabric of the present invention of the type illustrated in Figure 1 laminated to a face fabric 6. This is a typical way in which the composite fabric would be used for the production of a garment in practice. The face fabric 6 is typically laminated by the use of a layer of discontinuous adhesive, usually in a pattern of dots or lines according to conventional technology. The face fabric 6 is usually a woven nylon or polyester fabric.

Figure 4 shows a composite fabric including a layer 8 of a hydrophilic polyurethane which has been coated onto the sintered PTFE layer 4 by conventional coating technology. The hydrophilic coating is water-vapour-permeable and non-porous so that overall the composite fabric of this embodiment is not porous to air or gases. The hydrophilic layer protects against wetting out of the expanded PTFE membrane due to fats or oils or other surfactant materials from the skin of the wearer. Alternatively, the hydrophilic layer 8

may be applied onto the expanded PTFE membrane 2, or could be applied onto both layers 2, 4.

The invention will now be further described in relation to certain examples as follows.

EXAMPLES

The properties of the sprayed material (such as density and porosity) could be modified by varying the type of granular PTFE employed. PTFE grade 7A is unsintered. There exists a granular-type PTFE grade 9B which is a pre-melted sintered resin. Both grades may be milled to reduce the particle size as described herein prior to use. The solids content of the suspension could be varied in the range 0-100% grade 7A and 0-100% grade 9B depending on the desired properties of the final sintered porous PTFE layer. The thickness of the porous composite material comprising the layer of sintered porous PTFE on the expanded PTFE membrane was measured using a dial guage according to ASTM D461.

EXAMPLE 1 (Milled 7A resin)

1kg of Du Pont granular PTFE resin grade 7A which has previously been milled to an average particle size of 20 microns, 25g of Zonyl FSN-100 surfactant solution, 25g of Pluronic L121 and 1.6kgs of distilled water are blended together for 60 seconds using a

Waring blender to form a suspension. The resulting aqueous suspension was suitable for spray application.

Pluronic (trademark) L121 surfactant is a polyoxyethylene/polyoxypropylene block copolymer. The FSN-100 surfactant is a non-ionic perfluoroalkyl ethoxylate mixture. The FSN-100 surfactant solution consisted of a mixture of four parts FSN-100, three parts distilled water and three parts isopropyl alcohol (by weight).

An expanded PTFE membrane obtained from W.L. Gore & Associates Inc. having a nodes and fibril morphology of nominal pore size 0.1 microns with an approximate thickness of 60 microns prepared according to the teachings of US patent 3,953,566 was held under tension in an aluminium frame (20 inch x 20 inch outside, 16 inch x 16 inch inside). The frame contains a "tongue and groove" arrangement between the top and bottom plates to ensure that the membrane is held under tension throughout the process. The frames are held together using toggle clamps. The tensioned membrane contained within the internal dimensions of the frame is not in contact with any other surface.

48g of the aqueous suspension was sprayed onto one side of the membrane using a Binks BBR spray gun. The spray coated membrane held within the frame was dried in an oven at 65°C for 1 hour. The temperature was then increased over several hours to 350°C and

held at this temperature for 60 minutes to complete the baking process. After cooling, the toggle clamps are released and the porous composite material removed. The thickness of the composite was measured at 130-140 microns and therefore by subtraction, the layer of sintered porous PTFE sheet on the expanded membrane was 70-80 microns. The properties of this composite structure were then compared with the basic membrane alone i.e. uncoated, which has undergone the same thermal history. The results are shown in Table 1 (see test methodologies for test procedures).

It is clear from the results, that the sintered porous PTFE layer (100%7A) of the composite has no significant effect on the air flow rate (Gurley) of the material. This is due to the much higher air flow rate (lower Gurley value) of the sintered porous layer in comparison to the membrane. The composite retains significant breathability as shown by the MVTR values but shows a dramatic improvement in abrasion, fracture resistance and thermal dimensional stability.

EXAMPLE 2 (50%7A : 50%9B)

500g of Du Pont granular PTFE resin grade 7A, with an average particle size of 35 microns, 25g of Zonyl FSN-100 surfactant solution, 25g of Pluronic L121 and 1.3kgs of distilled water are blended together for 60 seconds using a Waring blender to form

a suspension. 500g of Du Pont granular PTFE resin grade 9B, which has previously been milled to an average particle size of 50 microns was added to the suspension and rebled for a further 60 seconds. The resulting aqueous suspension was suitable for spray application.

Pluronic (trademark) L121 surfactant is a polyoxyethylene/polyoxypropylene block copolymer. The FSN-100 surfactant is a non-ionic perfluoroalkyl ethoxylate mixture. The FSN-100 surfactant solution consisted of a mixture of four parts FSN-100, three parts distilled water and three parts isopropyl alcohol (by weight).

An expanded PTFE membrane having a nodes and fibrils morphology of nominal pore size 0.1 microns with an approximate thickness of 60 microns was held under tension in an aluminium frame (20inch x 20inch, 16inch x 16inch inside). The frame contains a "tongue and groove" arrangement between the top and bottom plates to ensure that the membrane is held under tension throughout the process. The frames are held together using toggle clamps. The tensioned membrane contained within the internal dimensions of the frame is not in contact with any other surface.

98g of the aqueous suspension was sprayed onto one side of the membrane using a Binks BBR spray gun. The spray coated membrane held within the frame was

dried in an oven at 65°C for 1 hour. The temperature was then increased over several hours to 350°C and held at this temperature for 60 minutes to complete the baking process. After cooling, the toggle clamps are released and the porous composite material removed. The thickness of the composite was measured at 230 microns and therefore by subtraction, the layer of sintered porous PTFE sheet on the expanded membrane was 170 microns. The properties of this composite structure were then compared with the base membrane alone i.e. uncoated, which has undergone the same thermal history. The results are shown in Table 2 (see test methodologies for test procedures).

It is again clear from the results, that the sintered porous PTFE layer (50%7A : 50%9B) of the composite has no significant effect on the air flow rate (Gurley) of the material. This is due to the much higher air flow rate (lower Gurley value) of the sintered porous layer in comparison to the membrane. The composite retains significant breathability as shown by the MVTR values but shows a dramatic improvement in abrasion, fracture resistance and thermal dimensional stability.

EXAMPLE 3 (Milled 7A)

1kg of Du Pont granular PTFE resin grade 7A which has previously been milled to an average particle size

of 20 microns, 25g of Zonyl FSN-100 surfactant solution, 25g of Pluronic L121 and 1.6kgs of distilled water are blended together for 60 seconds using a Waring blender to form a suspension. The resulting aqueous suspension was suitable for spray application.

The FSN-100 surfactant solution consisted of a mixture of four parts FSN-100, three parts distilled water and three parts isopropyl alcohol (by weight).

An expanded PTFE membrane having a nodes and fibrils morphology of nominal pore size 0.2 microns with an approximate thickness of 40 microns was held under tension in an aluminium frame (20inch x 20inch outside, 16inch x 16inch inside). The frame contains a "tongue and groove" arrangement between the top and bottom plates to ensure that the membrane is held under tension throughout the process. The frames are held together using toggle clamps. The tensioned membrane contained within the internal dimensions of the frame is not in contact with any other surface.

49g of the aqueous suspension was sprayed onto one side of the membrane using a Binks BBR spray gun. The spray coated membrane held within the frame was dried in an oven at 65°C for 1 hour. The temperature was then increased over several hours to 350°C and held at this temperature for 60 minutes to complete the baking process. After cooling, the toggle clamps are released and the porous composite material

removed. The thickness of the composite was measured at 100-110 microns and therefore by subtraction, the layer of sintered porous PTFE sheet on the expanded membrane was 60-70 microns.

The dimensional stability of the composite material to repeat solvent (isopropyl alcohol) washings was then compared with the base membrane alone i.e. uncoated, which has undergone the same thermal history. The results are shown in Table 3 and clearly illustrate the greater dimensional stability of the composite to solvent exposure.

TABLE 1 (Example 1)

SAMPLE	THICKNESS (microns)	MVTR (g/m ² /24hrs)	GURLEY (s/100cm ³) (s.deviation)	ABRASION (cycles to failure at 5psi)	FRACTURE HEIGHT Mem Impact (inches)	FRACTURE HEIGHT 100%7A Impact (inches)	% AREA Shrinkage(250°C)	% AREA Shrinkage (300°C)
Expanded Membrane	60	64,000	22.8 (1.0)	30,000	2	-	26.1	39.0
Expanded Membrane :100% 7A Composite	130-140	33,000	20.5(0.8)	> 500,000	5	8	4.1	6.8

TABLE 2 (Example 2)

SAMPLE	THICKNESS (microns)	MVTR (g/m ² /24hrs)	GURLEY (s/100cm ³) (s.deviation)	ABRASION (cycles to failure at 5psi)	FRACTURE HEIGHT Mem Impact (inches)	FRACTURE HEIGHT 50% 7A:50%9B Impact (inches)	% AREA SHRINKAGE (250°C)	% AREA SHRINKAGE (300°C)
EXPANDED MEMBRANE	60	64,000	22.8(1.0)	30,000	2	-	25.3	39.0
EXPANDED MEMBRANE :50%7A/ 50%9B Composite	230	28,000	21.5(0.8)	300,000	12.5	12.5	4.5	7.2

TABLE 3 (Example 3)

SAMPLE	THICKNESS (microns)	% AREA SHRINKAGE (IPA Wash 1)	% AREA SHRINKAGE (IPA Wash 2)	% AREA SHRINKAGE (IPA Wash 3)
Expanded Membrane	40	2.3	3.3	4.1
Expanded Membrane :100%7A Composite	100-110	0	0	0

EXAMPLE 4 (Milled 7A: 10% PFA)

450g of Du Pont granular PTFE resin - 7A, which has previously been milled to an average particle size of 15 microns, 50g of Du Pont PFA (perfluoroalkoxy), 12.5g of Zonyl FSN-100 surfactant solution, 12.5g of Pluronic L121 and 800g of distilled water are blended together for 60 seconds using a Waring blender to form a suspension. The resulting aqueous suspension was suitable for spray application.

Pluronic (trademark) L121 surfactant is a polyoxyethylene/polyoxypropylene block copolymer. The FSN-100 surfactant is a non-ionic perfluoroalkyl ethoxylate mixture. The

FSN-100 surfactant solution consisted of a mixture of four parts FSN-100, three parts distilled water and three parts isopropyl alcohol (by weight).

An expanded PTFE membrane having a nodes and fibril morphology of nominal pore size 0.1 microns with an approximate thickness of 60 microns was held under tension in an aluminium frame (20inch x 20inch outside, 16inch x 16inch inside). The frame contains a "tongue and groove" arrangement between the top and bottom plates to ensure that the membrane is held under tension throughout the process. The frames are held together using toggle clamps. The tensioned membrane contained within the internal dimensions of the frame is not in contact with any other surface.

38g of the aqueous suspension was sprayed onto one side of the membrane using a Binks BBR spray gun. The spray coated membrane held within the frame was dried in an oven at 65°C for 1 hour. The temperature was then increased over several hours to 350°C and held at this temperature for 60 minutes to complete the baking process. After cooling, the toggle clamps are released and the porous composite material removed. The thickness of the composite was measured at 160 microns and therefore by subtraction, the layer of sintered porous PTFE sheet on the expanded membrane was 100 microns. The properties of this composite structure were then compared with the base membrane

alone i.e. uncoated, which has undergone the same thermal history. The results are shown in Table 4 (see test methodologies for test procedures).

It appears from the results, that within the experimental error of the testing, the sintered porous PTFE layer of the composite has no significant effect on the air flow rate (Gurley) of the material. This is due to the much higher air flow rate (lower Gurley value) of the sintered porous layer in comparison to the membrane. The composite retains significant breathability as shown by the MVTR values but shows a dramatic improvement in thermal dimensional stability.

TABLE 4 (Example 4)

SAMPLE	Thickness (microns)	MVTR (g/m ² /24 hrs)	Gurley (s/100cm ³)	% Area Shrinkage (250°C)
Expanded Membrane	60	68,000	20.9(1.9)	18.1
Expanded Membrane 90%7A/10%PFA Composite	160	33,000	24.4(1.9)	3.6

() refer to typical one standard deviation values.

EXAMPLE 5: Fabric Lamination of Porous Composite Material

i) Two-layer Composite (Milled 7A)

Du Pont granular PTFE of resin - 7A, was milled to an average particle size of 20 microns. This was

then blended using a Silverson mixing head into an aqueous suspension consisting of the following:

- 5% Pluronic L121 surfactant
- 5% Zonyl FSN-100 surfactant solution
- 2.5% Carboxymethyl Cellulose 1% solution
- 160% Distilled Water

All % values are based on the weight of 7A resin. The Zonyl surfactant solution consisted of four parts Zonyl FSN-100 (non-ionic perfluoroalkyl ethoxylate) mixed with three parts distilled water and three parts isopropyl alcohol (by weight). Pluronic L121 is a trade name for a polyoxyethylene/polyoxypropylene block copolymer surfactant while Carboxymethyl Cellulose acts as a thickening agent. The resulting aqueous suspension was suitable for spray application.

An expanded PTFE membrane from W.L. Gore & Associates Inc. with a thickness of 30-40 microns and nominal pore size of 0.3 microns, formed the composite substrate. The membrane was firmly held in a stainless steel pin frame of dimensions 3ft x 9ft which provides a suitable base for spraying and subsequent baking.

The aqueous suspension was sprayed onto one side of the membrane using a Nordson Air-Assisted spraying system. After spraying, the coated membrane was dried in an oven for an hour at 110°C. The temperature was

then increased to 350°C and held at this temperature for 30 minutes to complete the baking process. After allowing to cool, the sheet of composite material was removed from the pinframe.

The thickness, airflow rate (Gurley test), maximum pore size and abrasion resistance of both the expanded membrane and the composite are as follows:

TABLE 5 (Example 5)

	Thickness microns	Gurley (s/100cm ³)	MVTR (g/m ² /24h)	Max. Pore (μm)	Abrasion resistance (cycles to failure at 1psi)
Membrane	33	13.7-17.6	70,000-73,000	0.415	1,000
Composite	142	14.2-17.8	20,000-23,000	0.643	650,000

The MVTR (moisture vapour transmission rate) test provides an indication of garment breathability.

The above results indicate that the composite retains significant breathability (MVTR values) and has dramatically increased abrasion resistance.

ii) Polyurethane Coating and Face Fabric

The next stage in the lamination process was to coat the porous non-expanded PTFE layer of the composite material with a hydrophilic polyurethane layer (about 10 micron thick) using conventional

doctor blade coating technology. The polyurethane coated surface is to be worn adjacent to the skin of the wearer in the finished garment. The polyurethane layer is moisture vapour permeable and air-impermeable. A tightly-woven nylon "Taslan" face fabric was then laminated to the expanded membrane side of the composite material using a discontinuous layer of adhesive applied from a dot-patterned gravure roller.

The primary properties of the porous composite fabric laminate material produced in this way, compared to that of a comparison expanded membrane fabric laminate prepared under similar conditions (but without the granular PTFE grade 7A layer) are as follows:

TABLE 6

	MVTR (g/m ₂ /24h)	Abrasion resistance (cycles to failure at 1 psi)	Fracture resistance (inches)
Expanded Membrane Laminate (comparison)	12,400	100,000	25
Expanded Membrane 100% 7A Laminate	4,800	> 1,000,000	35

From these results, it is clear that the composite fabric laminate of the present invention

retains significant breathability as shown by the MVTR values but also has a dramatic increase in the abrasion resistance compared to the expanded membrane fabric laminate. Higher MVTR values at good abrasion resistance could be obtained using thinner layers of sintered PTFE.

The abrasion test method in this Example is slightly different to that outlined in the Testing Methodologies with the porous unexpanded surface abraded and material failure in this case being considered to occur when one or more leaks are noted at a water pressure of 1psi during a 3 minute time period. Fracture height to failure was determined with the face fabric used as the uppermost "impact" surface.

Results from the Gurley airflow test show the laminates to be impermeable to air at a pressure drop of 4.88 inches of water.

TESTING AND PREPARATIVE METHODOLOGIES

(A) Preparation of PTFE grade 7A and 9B

TEFLON (trademark) granular-type PTFE fluorocarbon resin grades 7A and 9B are available from DuPont Speciality Polymers Division, Wilmington U.S.A. Grade 9B is a premelted sintered resin. The manufacturers product specification indicates an average density of 2.16, and an average particle size

of 35 microns (grade 7A) and 500 microns (grade 9B prior to milling). PTFE grade 7A was unsintered and was used as supplied or was milled in analogous manner.

Prior to use, the PTFE grade 9B was milled to a volume average particle size of about 50 microns by grinding an aqueous slurry thereof between grinding stones at room temperature as follows.

The PTFE grade 9B was mixed with water to form a slurry, and the slurry fed between closely spaced grinding surfaces of a grinding mill as disclosed in US-A-4841623, to crush and shear the pieces of PTFE into particles. The ground slurry was then filtered or centrifuged to separate the granular PTFE particles from water, and the separated finely ground particles were oven dried at from 125°C - 150°C.

(B1) Density

Unless otherwise stated, the density of the PTFE is determined by weighing a sample thereof in two different media, viz; air and water at room temperature. Water is a non-wetting medium for PTFE and consequently, the resulting density measurements refer to the porous PTFE. The weights were determined using an Avery VA124 analytical balance. The porous PTFE density is calculated as shown below:

(Weight in Air) (Density of Water at Room Temperature)

(Weight in Air - Weight in Water)

(B2) Porosity

% Porosity is determined from density measurements in wetting and non-wetting mediums i.e. isopropyl alcohol (IPA) and water respectively, as shown below:

$$\% \text{ Porosity} = \frac{(\text{Density in IPA} - \text{Density in Water}) \times 100}{(\text{Density in IPA})}$$

(C) Particle Size

Particle size of ground PTFE was determined as follows: using a magnetic stirrer and ultrasonic agitation, 2.5 grams of milled PTFE powder were dispersed in 60 ml isopropyl alcohol. (Ultrasonic Probe Model W-385, manufactured by Heat Systems-Ultrasonics, Inc.).

Aliquots of 4-6ml of the dispersed particles were added to approximately 250ml of circulating isopropyl alcohol in a Leeds & Northrup Microtrac X100 Particle Size Analyzer. Each analysis consisted of three 30-second runs at a sample circulation rate of 2 litres/minute during which light scattering by the dispersed particles is automatically measured and the particle size distribution automatically calculated from the measurements.

(D1) Pore Size Measurement (bubble point)

Pore size of polytetrafluoroethylene was determined from the bubble point, defined in this specification as the pressure required to blow the first bubble of air detectable by its rise through a layer of liquid covering the sample. A test device, as outlined in ASTM F316-80, was used consisting of a filter holder, manifold and pressure gauge (maximum gauge pressure of 275.8 kPa). The filter holder consisted of a base, a locking ring, an o-ring seal, support disk and air inlet. The support disk consisted of a 150 micron mesh screen and a perforated metal plate for rigidity. The effective area of the test sample was 8.0 plus or minus 0.5 cm².

The test sample was mounted on the filter holder and wetted with anhydrous methanol until clarified. The support screen was then placed on top of the sample and the top half of the filter holder was tightened in place. Approximately 2 cm of anhydrous methanol at 21°C was poured over the test sample. The pressure on the test sample was then gradually and uniformly increased by the operator until the first steady stream of bubbles through the anhydrous methanol were visible. Random bubbles or bubble stream of the outside edges were ignored. The bubble point was read directly from the pressure gauge.

The pore size of the test sample is related

to the amount of gas pressure required to overcome surface tension and is given by a form of the Washburn equation:

$$\text{bubble point (psi)} = K \cdot 4 \cdot Y \cdot \cos T / d$$

where K = shape factor

Y = surface tension of methanol

T = contact angle between pore and surface

d = maximum pore diameter.

(D2) Pore Size Measurements (Coulter Porometer)

The pore size of the materials is determined by a COULTER POROMETER II (trademark) which uses a liquid displacement technique. The sample is thoroughly wetted with a liquid of low surface tension and low vapour pressure e.g. COULTER POROFIL, such that all the pores have been filled with the liquid. The wetted sample is subjected to increasing pressure, applied by a gas source. As the pressure is increased, the surface tension of the liquid is finally overcome and the liquid is forced out of the pores. By monitoring the gas pressure applied to the sample and the flow of gas through the sample when liquid is expelled, a "wet" run is obtained. The sample is then tested "dry" without liquid in the pores and a "dry" run is obtained. By comparing both "wet" and "dry" runs, the maximum (also called the

bubble point), minimum and mean pore size can be calculated by the porometer using the Washburn equation, a form of which is shown in (D1).

In the case of laminated or composite materials, the sample gas pressure will be regulated by the material of smallest pore diameter which will effectively act as a pressure restrictor. Consequently, for composites of expanded PTFE membrane and porous granular PTFE, the pore size measurements will closely resemble that of the smallest pore diameter layer i.e. the expanded membrane.

(E) Abrasion Resistance

This test was carried out using a Martindale abrasion tester (described in J. Text.Inst. 1942:33, T151). Abrasion cloth, SM25 was abraded onto the expanded membrane side of all the materials, in a circular motion. The abrasion cloth was replaced at the start of each test and after each 100,000 cycles thereafter. The samples were tested at regular intervals for 1 minute at 5 psi water pressure and classified as a failure when more than one leak was noted. The 5psi water pressure was chosen as it is much greater than the water entry pressure of the sintered porous sheet. The general test method is described in Section (I).

(F) Fracture Resistance

5 ball bearings of approximate diameter 13mm and weight 22.8g were dropped from various heights onto the materials which in all cases were covered with a face fabric (MI 260). Ball drop tests on the composite materials were carried out with both porous sheet and membrane surfaces used as the "impact" side. The number of leaks from the 5 "ball impact" impressions was determined at 1 psi water pressure. Material failure was classified as the ball drop height at which 4 or more leaks were noted.

(G) Thermal Dimensional Stability

Pre-cut discs (109mm diameter) of the materials were placed in air-circulating ovens at 50°C and increased to 250°C and 300°C respectively, and held at these temperatures for 2 hours. After cooling to 50°C, the average diameter of the discs was noted and the % area shrinkage calculated.

(H) MOISTURE VAPOUR TRANSMISSION RATE (MVTR)(Potassium Acetate Method)

A description of the test employed to measure moisture vapour transmission rate (MVTR) i.e. water-vapour-permeability, is given below.

In the procedure, approximately 70ml of a solution consisting of 35 parts by weight of potassium

acetate and 15 parts by weight of distilled water was placed into a 133ml. polypropylene cup, having an inside diameter of 6.5cm at its mouth. An expanded polytetrafluoroethylene (PTFE) membrane having a minimum MVTR of approximately $85,000\text{g/m}^2/24\text{ hrs.}$ as tested by the method described in US Patent 4,862,730 to Crosby and available from W.L. Gore & Associates, Inc. of Newark, Delaware, was heat sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the solution.

A similar expanded PTFE membrane was mounted to the surface of a water bath. The water bath assembly was controlled at 23°C plus or minus 0.2°C , utilising a temperature controlled room and a water circulating bath. The sample to be tested was allowed to condition at a temperature of 23°C and a relative humidity of 50% prior to performing the test procedure. Three samples were placed so each sample to be tested was in contact with the expanded polytetrafluoroethylene membrane mounted over the surface of the water bath, and was allowed to equilibrate for at least 15 minutes prior to the introduction of the cup assembly.

The cup assembly was weighted to the nearest 1/1000g and was placed in an inverted manner onto the centre of the test sample.

Water transport was provided by the driving force

between the water in the water bath and the saturated salt solution providing water flux by diffusion in that direction. The sample was tested for 20 minutes and the cup assembly was then removed, and weighed again to within 1/1000g.

The MVTR of the sample was calculated from the weight gain of the cup assembly and was expressed in grams of water per square meter of sample surface area per 24 hours.

(I) WATER-RESISTANCE (SUTER TEST)

Samples of the present invention were tested for water-resistance using a modified Suter test apparatus, which is a low water entry pressure challenge. The test procedure is set out in BS3424, method 29C. Water was forced against the underside of a sample of 11.25cm diameter sealed by two circular rubber gaskets in a clamped arrangement. As appropriate, the sample was mounted with the hydrophilic coating downwards against the water, the expanded porous polytetrafluoroethylene membrane being uppermost. It is important that a leakproof seal is formed by the clamp mechanism, gaskets and sample. In deformable samples, the sample was overlaid by a reinforcing scrim (e.g. an open non-woven fabric) clamped over the sample. The upper side of the sample was open to the atmosphere and visible to the

operator. The water pressure on the underside of the sample was increased to the test pressure by a pump connected to a water reservoir, as indicated by a pressure gauge and regulated by an in-line valve. The upper side of the sample was visually observed for a period of three minutes for the appearance of any water which might be forced through the sample in the event of lack of water-resistance. Liquid water seen on the surface was interpreted as a deficiency in the water-resistance of the sample (i.e. a leak). The sample passed the test if no liquid water was visible on the upper side of the sample within the specified test period.

(J) AIR FLOW (Gurley numbers)

The permeability to air of the samples was measured by a Gurley densometer (ASTM D72658) manufactured by W & L.E. Gurley & Sons. Results are reported in terms of Gurley number which is the time in seconds for 100 cm of air to pass through one square inch of the sample under a pressure of 4.88" of water head pressure. This measurement can be converted into metric permeability units ($\text{cm}^3\text{cm}/\text{sec} \cdot \text{cm}^2\text{cm.Hg}$) by the following formula: thickness of sample $\times 0.0432/\text{Gurley number}$. The lower the Gurley number, the higher the air permeability.

CLAIMS

1. A composite fabric which comprises a laminate comprising:
 - a sheet of expanded polytetrafluoroethylene (PTFE) membrane; and
 - a layer of non-expanded porous polytetrafluoroethylene (PTFE) attached to the expanded membrane sheet.
2. A fabric according to claim 1 wherein the layer of non-expanded porous PTFE is a sintered PTFE network.
3. A fabric according to claim 1 or 2 wherein the layer of non-expanded porous PTFE is a sintered porous PTFE formed from PTFE particles, comprising granular-type PTFE, fused together such as to form a porous integral network of interconnected particles.
4. A fabric according to claim 3 wherein the granular-type PTFE is modified by the inclusion of a fluorinated organic polymer comonomer.
5. A fabric according to claim 3 wherein the sintered non-expanded porous PTFE layer comprises particles of granular-type PTFE and unsintered fine powder PTFE fused to form said network.

6. A fabric according to claim 5 wherein the unsintered fine powder PTFE is modified by the inclusion of hexafluoropropylene comonomer.

7. A fabric according to claim 4 wherein the sintered non-expanded porous PTFE layer comprises particles of granular-type PTFE and particles of thermoplastic fluorinated organic polymer fused to form said network.

8. A fabric according to claim 7 wherein the thermoplastic fluorinated organic polymer is fluorinated ethylene-propylene copolymer, or a copolymer of tetrafluoroethylene and perfluoropropyl vinyl ether.

9. A fabric according to claim 3 wherein the sintered non-expanded porous PTFE layer comprises particles of granular-type PTFE and particles of low molecular weight irradiated PTFE fused to form said network.

10. A fabric according to claim 2 or 3 wherein the layer of sintered porous PTFE is formed on the expanded PTFE membrane and integrally attached hereto.

11. A fabric according to any of claim 2 to 10 in the form of a multiple layer structure, which comprises a layer of sintered porous PTFE formed between two expanded PTFE membranes and attached thereto.

12. A fabric according to any of claims 2 to 10 in the form of a multiple layer structure, which comprises layers of sintered porous PTFE formed on either side of an expanded PTFE membrane and attached thereto.

13. A fabric according to any preceding claim wherein the expanded PTFE membrane has a thickness of 30 to 500 microns; and the layer of non-expanded porous PTFE has a thickness of 25 to 500 microns.

14. A fabric according to any preceding claim wherein the porosity of the expanded PTFE membrane is in the range 70 to 95%.

15. A fabric according to any preceding claim wherein the expanded PTFE membrane has been formed into fibres and woven into a fabric.

16. A fabric according to any preceding claim wherein the density of the layer of non-expanded porous PTFE is in the range 0.6 to 1.5g/cm³.

17. A fabric according to any preceding claim wherein the non-expanded porous PTFE layer is impregnated with a hydrophobic impregnant.

18. A fabric according to claim 17 wherein the hydrophobic impregnant is a perfluoroalkyl acrylate or methacrylate.

19. A fabric according to any preceding claim which further comprises a layer of a hydrophilic polyurethane applied to either the expanded PTFE membrane or to the non-expanded PTFE layer, or applied to both.

20. A fabric according to any preceding claim which exhibits dimensional stability at 250°C.

21. A fabric according to any preceding claim having a water-vapour-permeability of at least 3000 g/m²/day

22. A fabric according to any preceding claim which further comprises a liner attached thereto.

23. A fabric according to any preceding claim which further comprises a face fabric attached thereto.

24. A garment which comprises a composite fabric of any preceding claim.

25. Footwear which comprises a composite fabric of any of claims 1 to 23.

26. A hat, glove, cover, covering or hanging which comprises a composite fabric of any of claims 1 to 23.

27. A method of forming a composite fabric which comprises;

- providing an expanded PTFE membrane; and
- forming thereon a layer of sintered porous PTFE attached to the expanded PTFE membrane, the sintered porous PTFE being formed from PTFE particles, comprising granular-type PTFE, fused together such as to form a porous integral network of interconnected particles.

28. A method according to claim 27 wherein the layer of sintered porous PTFE is formed by coating the expanded PTFE membrane with a liquid dispersion comprising particles of granular-type PTFE and baking at an elevated temperature such as to form a porous integral network.

29. A method according to claim 28 wherein the granular-type PTFE particles include unsintered granular type PTFE of mean particle size 10 to 20 microns.

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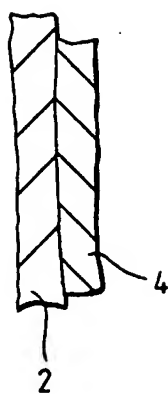


FIG. 1

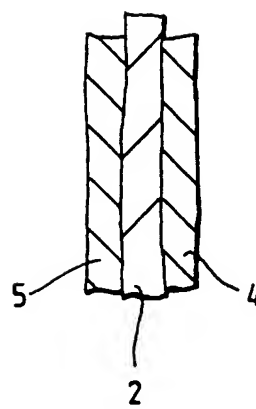


FIG. 2

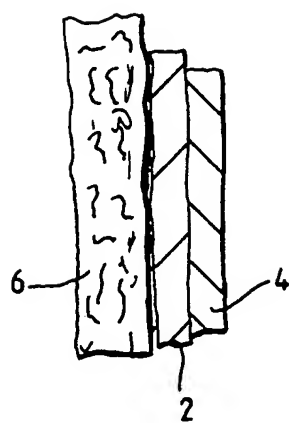


FIG. 3

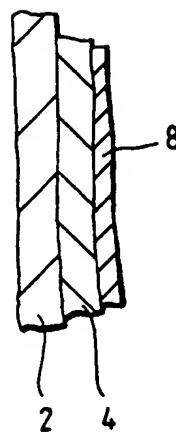


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 98/01867

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B32B 5/32, B32B 27/00, A41D 31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B32B, C08J, D06N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9640510 A1 (W.L. GORE & ASSOCIATES (UK) LTD.), 19 December 1996 (19.12.96), claims 1-14, 17-18, pages 14, 18, 22-23	1-29
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A	US 5418054 A (KWOK K. SUN), 23 May 1995 (23.05.95), column 4, line 50 - line 61, abstract	1-29
	--	
A	US 3775170 A (SOLOMON ROSENBLATT), 27 November 1973 (27.11.73), column 2, line 38 - line 51, claim 1	1-29
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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| <ul style="list-style-type: none"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | <ul style="list-style-type: none"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family |
|---|--|

Date of the actual completion of the international search

Date of mailing of the international search report

6 October 1998

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 98/01867

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4194041 A (ROBERT W. GORE ET AL), 18 March 1980 (18.03.80), column 4, line 54 - column 5, line 6, abstract</p> <p style="text-align: center;">-- -----</p>	1-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

27/07/98

International application No.

PCT/GB 98/01867

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9640510 A1	19/12/96	AU 5906896 A	30/12/96
		EP 0830249 A	25/03/98
		GB 2311237 A	24/09/97
		GB 9511518 D	00/00/00
		GB 9712699 D	00/00/00
		GB 9606823 D	00/00/00
US 5418054 A	23/05/95	CA 2156630 A	29/09/94
		DE 69305658 D,T	20/03/97
		EP 0689500 A,B	03/01/96
		JP 8507732 T	20/08/96
		WO 9421453 A	29/09/94
US 3775170 A	27/11/73	DE 1604462 A,B	14/01/71
		FR 1475033 A	00/00/00
		GB 1136862 A	00/00/00
		JP 49029888 B	08/08/74
		US 3497256 A	24/02/70
US 4194041 A	18/03/80	AU 524128 B	02/09/82
		AU 4636079 A	03/01/80
		BR 7903470 A	05/02/80
		CA 1112551 A	17/11/81
		DE 2925318 A,C	17/01/80
		DE 2954263 C	06/03/86
		DK 259479 A	30/12/79
		FR 2429666 A,B	25/01/80
		GB 2024100 A,B	09/01/80
		HK 63183 A	09/12/83
		JP 1388850 C	14/07/87
		JP 55007483 A	19/01/80
		JP 60039014 B	04/09/85
		NL 186589 B,C	01/08/90
		NL 7904783 A	03/01/80
		SE 445815 B,C	21/07/86
		SE 7902163 A	30/12/79
		ZA 7903253 A	27/08/80